

LEACHATES FROM DECOMPOSING LEAVES

II. INTERACTION WITH SOIL-FORMING MATERIALS¹

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ABSTRACT

The capacities of leachates from decomposing leaves of deciduous trees to attack calcareous and non-calcareous parent materials (taken from the C horizons of a brown forest and a podsol soil respectively), and soil from the B horizon of a podsol have been examined. The changes in the composition of extracts obtained in this way when brought into contact with other soil materials also have been studied. Attempts have been made to ascertain the chemical form or forms in which iron exists in the leachates and in the extracts obtained by the action of these leachates on soil and parent material.

Leachates from both beech and maple leaves extracted iron from both parent materials and calcium from the calcareous till, but lost the latter element to the podsol parent material.

The solution obtained by action of beech leachate on soil from the B horizon of a podsol was more acidic and had a greater capacity to extract iron from the parent materials than had the original beech leachate.

Most of the iron present in leachates from maple leaves was not removed from solution by passage over a cation and an anion exchange resin, but most of the iron added to such leachates as iron salts was retained by these resins. When iron salts were added to maple leachate a major part of the iron so added was not reactive with 2,2'-dipyridyl. Most of the iron extracted by maple leachate from the sandy parent material migrated toward the negative pole under electrodialysis.

The development of the podsol profile has been attributed to the action of acidic substances derived from decomposition of the organic materials in the A₀₀ and A₀ layers (7). Attempts have been made to determine the mechanism of the process by laboratory studies employing colloidal humus extracted from soil (3, 4). Organic acids of low molecular weight, such as might be produced in the decomposition of organic matter, also have been used in such researches (5, 8).

The present investigation has sought to obtain information on the mechanism of the podsolization process through the use of solutions obtained by the leaching action of natural precipitation on decomposing leaves (1, 10). The capacity of such leachates to attack calcareous and non-calcareous parent materials and soil from the B horizon of a ground-water podsol has been examined. The changes in composition of extracts obtained in this way, when they were brought into contact with other soil materials, also have been studied. Attempts have been made to ascertain the chemical form or forms in which iron exists in the leachates and extracts. The present constitutes a progress report with special emphasis on the behaviour of iron.

EXPERIMENTAL MATERIALS

The parent materials used were taken from the C horizons of the Grenville (St. Bernard) and the Ste. Sophie soils, representatives of the brown forest and the podsol groups, respectively. The vegetative cover

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at the sampling sites was forest, the most abundant species at the Grenville site being sugar maple (*Acer Saccharum*), that at the Ste. Sophie site American beech (*Fagus grandifolia* Ehrh.). The sites were situated in the Morgan Arboretum at Macdonald College, Que. They were located with the aid of a soil map prepared by P. Lajoie of the Canada Soil Survey Service (*unpublished*). The samples were taken at a depth of about 30 inches. The material obtained at the Grenville site was a calcareous gravelly loam till derived mainly from dolomitic rocks of the Beekmantown formation. The Ste. Sophie sample consisted mainly of fine sand which had been water-deposited over Champlain clay. More complete descriptions of these soils may be found in the report by Lajoie and Stobbe (9).

The ground-water podsol material, hereinafter designated B-soil, was collected under mixed beech-hemlock cover in the Morgan Arboretum, where this kind of profile occurs as the imperfectly drained member of the St. Amable complex (9). The sample was taken from a depth of 18 to 22 inches. In place, this material had the consistence and colour of orterde.

The samples collected were allowed to air-dry, after which representative portions were crushed and screened over a 1.0 mm. sieve. Only that portion passing this sieve was used in the experiments described below. The pH values after air-drying and sieving were 7.89, 5.15 and 4.97 for the Grenville, Ste. Sophie and B-soil materials, respectively.

The leachates employed were obtained as described previously (1, 10). Those used in the present study were derived from leaves of American beech (*Fagus grandifolia* Ehrh.) growing on Ste. Sophie soil, and from leaves of sugar maple (*Acer Saccharum* Marsh) growing on Grenville soil.

The leachates used in the extraction of the Grenville and Ste. Sophie soil-forming materials were collected through the growing season of 1949 from leaves of the 1948 crop which had been exposed to leaching continuously from the end of the 1948 leaf-fall period. Successive collections of leachates were combined to form a batch. Six batches of each kind of leachate were obtained and numbered 1 to 6 as collected. Prior to experimental use the batches of leachates were stored in large galvanized-iron cans coated with asphalt paint in a refrigerated room at about 6° C. The cans were covered and the room was lighted only when materials were being placed in or removed from it.

The leachates used in the experiments with the B-soil, and those employed in the investigation of the chemical forms of iron in leachates and extracts—with the exception of the electrodialysis experiment, for which Batch 1 maple leachate (1949 collection) was used—were collected in 1950 from leaves of the 1949 crop. These leaves had been exposed only from early spring 1950, and they were inoculated by spraying with soil suspensions obtained by shaking with water either A₀ material (Ste. Sophie) or A₁ soil (Grenville), taken from the sites where the leaves were collected. The suspension from the A₀ material was applied to the beech leaves, that from the A₁ to the maple leaves.

EXPERIMENTAL METHODS

In the extraction of the two parent materials a 5-gm. sample was placed in a 3-1 conical flask, 750 ml. of leachate added, and the stoppered

flask placed on a horizontally-reciprocating shaker operated at the rate of 30 strokes per minute. Samples of the supernatant solution were withdrawn daily from the continuously shaken mixture for analysis for iron content, shaking being continued until the latter attained a maximum value. This maximum generally was followed by a decline. The extraction time for leachates of different batches varied from 4 to 10 days. It was approximately the same for beech and maple leachates of the same batch, or collection period, and for both parent materials. The time required to reach maximum iron content increased from Batch 1 (collected April 18 to May 9) to Batch 5 (collected September 19 to September 30), then decreased for Batch 6 (collected October 5 to November 12). After the extraction time for a given batch of leachate had been established other samples were extracted for the same period to obtain the solutions which were analysed.

In the extraction of B-soil, also in the preparation of extracts from the two parent materials for reaction with B-soil, a uniform extraction time of 3 days was employed. In case of extracts reacting with soil materials, sample weights of 3 gm. each were shaken with 450 ml. of extract, the proportion of soil material to solution remaining as above.

Prior to analysis all extracts were centrifuged at 2400 r.p.m. for 30 minutes. Aliquot portions of the supernatant solutions so obtained then were evaporated to small volume and oxidized with a nitric-sulphuric-perchloric acid mixture; leachates were treated similarly in these respects. The oxidized solutions were analysed for iron or for iron, aluminum and calcium. Iron was determined either as the 2,2'-dipyridyl complex, after adding an acetate buffer at pH 4.6 and after reduction with hydroxylamine (6, 11) or in the ferric form along with aluminum using ferron (2). Calcium was estimated by permanganate titration of the oxalate (12). pH measurements were made with a Beckman model G pH meter using a glass-calomel electrode assembly. Electrodialysis was performed in a Mattison-type unit. The resins used in the ion-exchange experiments were Duolite C-3 (cation) and Duolite A-2 (anion). These resins were used (*a*), in the unadjusted H- and OH- forms and (*b*), as the mixed ammonium-hydrogen and acetate-hydroxyl forms produced by leaching with ammonium acetate-acetic acid buffers adjusted to a given pH until the effluent solution had the same pH as the influent.

RESULTS AND DISCUSSION

Extraction of Parent Materials

The results of the experiments to determine the extractive power of leachates when shaken with parent materials are summarized in Table 1.

Examination of the data shows that the pH of the extracts usually was higher than that of the leachates. Also, iron invariably was extracted from both parent materials, and calcium extracted from the Grenville but usually lost to the Ste. Sophie material. In addition, it is seen that the beech leachates invariably lost aluminium to both parent forming materials, whereas the maple leachates nearly always extracted this element from both. The changes in calcium content of the leachates are of the kind which would be expected from the nature of the materials extracted. The variations in

TABLE 1.—CHANGES IN pH AND IN AMOUNTS OF IRON, ALUMINIUM AND CALCIUM (IN MILLIMOLES PER LITRE) ON INTERACTION OF LEACHATES WITH PARENT MATERIALS

| Parent materials | | Ste. Sophie | | | | Grenville | | | |
|------------------|-----------|-------------|--------|--------|--------|-----------|--------|--------|--------|
| Leachate | Batch No. | pH | Fe | Al | Ca | pH | Fe | Al | Ca |
| Beech | 1 | — | +0.020 | -0.177 | +0.004 | — | +0.030 | -0.408 | +0.785 |
| | 2 | -0.08 | +0.036 | -0.075 | 0 | +0.55 | +0.066 | -0.174 | +0.631 |
| | 3 | +0.29 | +0.024 | -0.158 | 0 | +1.03 | +0.107 | -0.433 | +0.702 |
| | 4 | -0.08 | +0.042 | -0.131 | -0.042 | +0.14 | +0.077 | -0.339 | +0.697 |
| | 5 | +0.26 | +0.042 | -0.062 | -0.006 | -0.62 | +0.227 | -0.173 | +0.896 |
| | 6 | +0.10 | +0.012 | -0.495 | +0.021 | +0.53 | +0.167 | -1.184 | +0.378 |
| Maple | 1 | — | +0.025 | -0.003 | -0.020 | — | +0.122 | -0.065 | +0.203 |
| | 2 | +0.23 | +0.048 | +0.074 | -0.034 | +1.23 | +0.135 | +0.340 | +0.464 |
| | 3 | -0.05 | +0.036 | +0.411 | +0.074 | +0.84 | +0.124 | +0.172 | +0.377 |
| | 4 | +1.37 | +0.039 | +0.049 | -0.039 | +0.80 | +0.150 | +0.086 | +0.188 |
| | 5 | +1.42 | +0.030 | +0.104 | -0.019 | +0.55 | +0.105 | +0.074 | +0.160 |
| | 6 | +0.77 | +0.021 | +0.217 | -0.053 | +0.97 | +0.151 | -0.284 | +0.186 |

aluminium content seem to be related to the botanical origin of the leachate used. At present no explanation of the differential behaviour of the leachates in this respect can be advanced.

Reaction of Extracts with Soil Materials

The results of the experiments conducted with extracts are recorded in Table 2. In this table the changes in the content of the three elements determined are given in terms of percentages gained or lost by the extract (content in extract = 100 per cent).

TABLE 2.—CHANGES IN EXTRACTS ON CONTACT WITH A SECOND SOIL MATERIAL

| | Difference in pH | Percentage changes | | |
|---|------------------|--------------------|-----|------|
| | | Fe | Al | Ca |
| Extracts from Ste. Sophie parent material reacting with B-soil: | | | | |
| Beech extract | -0.66 | +25 | - 8 | -29 |
| Maple extract | -0.72 | +37 | -12 | -18 |
| Extracts from Grenville parent material reacting with B-soil: | | | | |
| Beech extract | -0.44 | -39 | +30 | -62 |
| Maple extract | -0.54 | - 8 | 0 | -17 |
| Extracts from B-soil reacting with Ste. Sophie parent material: | | | | |
| Beech extract | -0.10 | +650 | +28 | -67 |
| Maple extract | -0.06 | +81 | + 9 | - 6 |
| Extracts from B-soil reacting with Grenville parent material: | | | | |
| Beech extract | +1.43 | +2350 | +14 | +402 |
| Maple extract | +0.57 | +469 | -12 | +43 |

Examination of this table shows that the pH of the extracts decreased in all instances except when extracts from B-soil reacted with Grenville parent material, in which case a rise in pH would be anticipated. Where decreases in pH occurred they were accompanied by loss of calcium, but there seemed to be no consistent relationship between the decline in pH and the amount of calcium lost. Major decreases in pH occurred on reaction with B-soil. It is suggested that the leachates may have extracted acidic substances from this material, or, alternatively, that new acidic substances or acidic groups were produced in the interaction of the extract with the B-soil.

It is seen also that extracts from Grenville material lost iron to B-soil, whereas all other extracts gained in iron content, especially those from the B-soil. The increased capacity for iron uptake of beech leachate after contact with B-soil, and the large difference from maple leachate in this respect, are especially noteworthy. No adequate explanation of this behaviour, or of the apparently erratic and generally small changes in aluminium content of the extracts, can be advanced at present.

Forms of Iron Present in Leachates and in Extracts

It was postulated that the leachates and extracts under investigation might contain the following forms of iron: (a) ferrous or ferric ions, or both, (b), these ions in complexes retaining a positive charge or having acquired a negative charge, (c), in complexes or compounds having little or no effective charge. On the basis of this hypothesis it seemed desirable to investigate the possibility of separation of different forms of iron by means of ion exchange resins.

An ion-exchange procedure was applied to the investigation of the forms of iron present in maple leachates collected July 15 and August 2, 1950. Aliquots of 100 ml. each of leachate were passed successively through pairs of cation- and anion-exchange columns. Thus, one aliquot was passed through a pair of columns in which the cation-exchanger came first, a second aliquot through another pair in which the anion-exchanger preceded the cation-exchanger. The volumes of resin used in the columns were 15.5 and 14.0 ml. of the cationic and anionic forms, respectively. The cationic resin was used in the H-form, the anionic in the OH-form. The total iron contents of the leachates used were 0.116 and 0.136 mgm. per ml., respectively. The results obtained are reported in Table 3. One aliquot of the July 15th leachate and five successive aliquots of the August 2nd leachate were passed through each pair of exchange columns.

The most notable features of the data presented in this table seem to be: (a) the rather small proportion of the total iron retained; (b) the relatively uniform amounts of iron withdrawn from the leachates, and (c) the fact that the first resin passed removed the greater part of the iron lost from the leachate regardless of whether this was the cation or the anion resin. The last-mentioned characteristic suggests that adsorption, or precipitation, rather than ion-exchange is the principal cause of iron retention by these resins. The fact that about half the iron passed both resins suggests that a part at least of the leachate iron may be relatively freely mobile in the soil profile.

TABLE 3.—RETENTION OF IRON OF MAPLE LEACHATES BY ION-EXCHANGE RESINS

| Leachate | Milligrams iron retained by individual resins | | | | Per cent iron retained by resin pairs | |
|---|---|-------|--------------|-------|---------------------------------------|--------------|
| | Cation-anion | | Anion-cation | | Cation-anion | Anion-cation |
| <i>Collected July 15—</i> Aliquot 1 | 0.053 | 0.016 | 0.077 | 0.000 | 60 | 66 |
| <i>Collected August 2—</i> Aliquot 1 | 0.047 | 0.007 | 0.044 | 0.017 | 40 | 45 |
| 2 | 0.034 | 0.021 | 0.037 | 0.017 | 40 | 40 |
| 3 | 0.015 | 0.026 | 0.050 | 0.012 | 30 | 45 |
| 4 | 0.050 | — | 0.058 | 0.010 | — | 50 |
| 5 | 0.046 | 0.020 | 0.072 | 0.028 | 48 | 73 |

The data obtained in this initial experiment with the ion exchange resins being somewhat disappointing, it was thought possible that more encouraging results might be secured with solutions containing larger amounts of iron, more of which might be in cationic form. Therefore a further experiment was carried out in which maple leachate enriched with iron by addition of either ferrous or ferric sulphate was used. The leachate employed was collected on July 15, 1950. It contained 0.116 mgm. total iron before enrichment, and 1.065, and 1.050 mgm. after addition of ferrous sulphate and ferric sulphate, respectively. (These latter concentrations of iron are of similar order of magnitude to those obtained by extraction of soil materials, for example, the total iron concentration of an extract used in the next experiment to be reported was 0.960 mgm. per 100 ml.). Passage of the iron-enriched solutions through the resin columns began approximately thirty minutes after the iron salts were added. Here, as before, the resins were in the hydrogen and hydroxyl forms, respectively. The initial flow rate through the columns was 3 ml. per minute, but, as these solutions continued to pass through the columns, this rate was considerably reduced regardless of which resin was in the first position. Accumulation of a dark-coloured material near the top of the anion column was observed when this was the first in line. Such accumulation could not be detected—because of the colour of the resin itself—when the cation column was in this position. The results obtained are given in Table 4, as percentages of the added iron retained by each column and passing into the final effluent. In making these calculations it was assumed that the behaviour on the exchange resins of the original iron of the leachate was unaffected by the addition of the iron salts. That is, the amounts of iron retained on passing the unmodified leachate over them (Table 3) have been subtracted from those retained when the enriched leachates were used and the differences calculated as percentages of the amounts of iron added as salts.

Inspection of Table 4 shows that the partition of the added iron was, in fact, different from that of the original leachate iron. The most notable difference is that but a small proportion of this iron escaped retention by

TABLE 4.—PARTITION OF ADDED IRON ON EXCHANGE RESINS

| First column | Form of iron added | Percentage of added iron | | |
|--------------|---|---------------------------|--------------------------|-------------------|
| | | Retained on cation column | Retained on anion column | In final effluent |
| Cation | FeSO ₄ | 87 | 2 | 11 |
| Cation | Fe ₂ (SO ₄) ₃ | 93 | 7 | 0 |
| Anion | FeSO ₄ | 13 | 80 | 7 |
| Anion | Fe ₂ (SO ₄) ₃ | 8 | 88 | 4 |

TABLE 5.—PARTITION OF IRON OF EXTRACTS AND OF LEACHATE ON EXCHANGE RESINS

| Influence solution | Initial pH | Total iron mgm./100 ml. | Percentage distribution of iron | | | pH of final effluent |
|--|---------------|----------------------------|--|--|----------------------|----------------------------|
| | | | Retained on first (cation) column | Retained on second (anion) column | In final effluent | |
| <i>Part A. pH of resins not adjusted</i> | | | | | | |
| Extract from Grenville by maple leachate of July 15, 1950 | — | 0.960 | 21 | 4 | 75 | — |
| <i>Part B. pH of resins adjusted</i> | | | | | | |
| Maple leachate of July 15, 1950 | 6.3 | 0.096 | Nil | 32 | 68 | 6.7 |
| Extract from Grenville by this leachate | 6.8 | 0.720 | Nil | 29 | 71 | 5.9 |
| Extract from Ste. Sophie by this leachate | 6.6 | 0.200 | 19 | 86 | —5 | 5.6 |

both resins. However, it is once more observed that, regardless of their relative positions, the first resin encountered retained the major part of the iron added to the leachate.

In the next experiments an attempt was made to adjust the pH values of both cation and the anion resin to that of the leachate or extract passed over them. This was done by preparing ammonium acetate buffer solutions—from ammonia solution and acetic acid—having pH values essentially the same as those of the leachates or extracts to be investigated. These buffer solutions were passed through the resin columns until the pH of the effluent was the same as that of the influent buffer. After this preparation of the columns the leachate or extract to be studied was added. The pH of the effluent solution (leachate or extract) from the first column was not readjusted before it entered the second column. The results of these experiments are reported in Table 5, which also contains data obtained when the pH of the resins was not adjusted.

Comparison of Part A of Table 5 with Table 4—pH of resins not adjusted in either instance—shows that the iron extracted from Grenville parent material behaves quite differently from that of the iron of iron salts added to the same leachate. Thus, 75 per cent of the extracted iron passes both exchange columns whereas more than this proportion of the iron added as iron salts was retained by the resins. It may be noted that reversal of the positions of the cation and anion columns made no difference in the proportion of iron extracted from the Grenville material which passed both resins.

Table 5 shows also that adjustment of the pH of the resins made no considerable difference in the retention of iron extracted from the Grenville material.

In Part B of Table 5 it is seen that the behaviour of iron extracted from the Ste. Sophie parent material—by another portion of the same leachate as used on the Grenville material—was radically different from that of the iron extracted from the latter, by far the major part of the iron of the former extract being retained by the anion column. Interpretation of this difference in the behaviour of the extracts obtained from the two parent materials is rendered difficult by the observation that the Grenville extract remained slightly turbid after centrifugation, and that some of the suspended material passed both columns. The amount of iron associated with the suspended material in the final effluent is not known.

Comparison of the results obtained after addition of iron salts (Table 4) with those obtained with unmodified leachates (Table 3) and with iron-enriched extracts (Table 5), shows that addition of inorganic iron salts led to behaviour on ion-exchange columns distinctly different from that of leachates and of extracts in respect of retention of iron by the resins. It is possible that the differences shown by added as compared to extracted iron may be due, in part, to the more extended time of contact with the leachate in the case of the latter, namely three days as compared with one-half hour for the iron salts. It is apparent also, from the data of Table 5, that the kind of parent material reacting with maple leachate had a very marked effect on the mobility of the iron over ion-exchange resin surfaces. It is perhaps unnecessary to emphasize that the mobility of iron over such surfaces does not necessarily reflect the fate of leachate or of extract iron moving over the surfaces in soil profiles. Nevertheless, the variations in behaviour toward the exchange resins must represent real differences in the physico-chemical constitution of these iron-containing solutions, and the results obtained are suggestive of the desirability of further investigation of such solutions.

In general, the results of these experiments with ion-exchange resins suggest that clean-cut separations of cationic, anionic and neutral forms of iron are unlikely to be obtained, at least with the resins and the techniques here employed.

Partition of Iron by Electrodialysis

An extract obtained by shaking maple leachate of Batch 1 with Ste. Sophie parent material was subjected to electrodialysis. A 3-cell apparatus of the Mattson type fitted with parchment membranes was employed.

TABLE 6.—FRACTIONATION BY ELECTRODIALYSIS OF THE IRON IN A MAPLE LEACHATE EXTRACT FROM STE. SOPHIE PARENT MATERIAL

| Fraction | Iron, mgm. | Per cent of total iron |
|--------------------------|------------|------------------------|
| Cathode cell solution | 0.17 | 6.7 |
| Cathode cell precipitate | 1.48 | 58.5 |
| Central cell solution | 0.16 | 6.3 |
| Central cell precipitate | 0.50 | 19.8 |
| Anode cell solution | 0.13 | 5.1 |
| Anode cell precipitate | 0.09 | 3.6 |

The solutions in the anodic and cathodic cells were replaced with distilled water on the second and the fourth days after starting dialysis. The experiment was discontinued on the fifth day, the amperage having returned to the original value and gas evolution at the electrodes being no longer appreciable. The distribution of iron obtained is shown in Table 6. In securing this information the iron was determined by the dipyrldyl method.

The data of Table 6 indicate that the major part of the iron in this extract is positively charged. However, the degree to which this form of iron may have been derived, during the prolonged period of dialysis, from the decomposition of complexes or compounds of iron is unknown. The precipitate in the central cell formed mainly at the membrane on the anodic side of this cell. This fact, together with the observation that a small amount of iron was able to migrate into the anode cell, indicated that a considerable proportion of the iron present was associated with anionic material.

Partition of Iron by Chemical Action

In these experiments, the capacity of iron present in or added to maple leachate to react directly with 2,2'-dipyrldyl, or with this reagent after the addition of hydroxylamine hydrochloride, was measured. It was thought that the results obtained might provide information on the occurrence in these solutions of ferrous and ferric iron and, indirectly, on the presence or absence of very stable complexes or compounds of iron in the original leachate and in the leachate after addition of inorganic salts of iron.

The maple leachate used in these experiments was collected during the latter part of the 1950 season, had been in cool storage in the dark for some time, and was exposed to laboratory conditions of light and temperature for 5 days before use. Ferrous and ferric sulphates were added, separately, and each at two concentrations, to 25 ml. aliquots of the leachate. The time from addition of the iron salts to the addition of the reagents for estimation of iron was about 30 minutes in all instances. Aqueous solutions of the iron salts were prepared at the same time and analysed similarly. The leachate employed contain 0.039 mgm. of iron per 25 ml., none of which reacted with dipyrldyl after the leachate had been exposed to labora-

TABLE 7.—RECOVERY OF IRON ADDED TO MAPLE LEACHATE

| Treatment | Iron concn., mgm./25 ml. | Percentage recovery | | | |
|-----------------------|-----------------------------|---------------------|--------|-------------------|--------|
| | | Aqueous solution | | Leachate solution | |
| | | Ferrous | Ferric | Ferrous | Ferric |
| Without hydroxylamine | 0.022 | 64 | 0.0 | 27 | 23 |
| With hydroxylamine | | 100 | 100 | 41 | 32 |
| Without hydroxylamine | 0.087 | 84 | 5 | 48 | 23 |
| With hydroxylamine | | 100 | 100 | 49 | 44 |

tory conditions for 5 days (7.7 per cent of its iron content was reactive to dipyrindyl immediately after removal from cool storage). The data obtained are presented in Table 7.

Inspection of these results indicates, first, that added iron, whether ferrous or ferric, reacted with the leachate to form complexes or compounds which did not interact with 2,2'-dipyridyl to produce a coloured complex, the recoveries from the iron-enriched leachates in all instances being less than from the aqueous solutions. Further, it appears that the extent of this type of reaction was increased by increasing the concentration of iron in the leachate solution, and that ferrous iron was somewhat less reactive in this respect than ferric.

CONCLUSIONS

It has been shown that leachates produced from decomposing beech and maple leaves by natural precipitation are capable of extracting iron from both water-deposited sand and calcareous till taken from the C horizons of a podsol and a brown forest soil, respectively. The beech leachates lost aluminium to both these soil-forming materials whereas the maple leachates nearly always extracted this element. Both kinds of leachates extracted calcium from the till and usually lost it to the acidic sand. In general, the pH of the extracts was higher than that of the leachates.

The changes in pH and in content of the same three elements when leachate-extracts obtained from one soil material were allowed to react with a second have been determined. The most pronounced effects were noted when the extract was prepared by interaction of beech leachate with soil from the B horizon of a sandy ground-water podsol. This extract was more acidic than the original leachate and it possessed a greatly enhanced capacity for extraction of iron from C-horizon material.

Attempts have been made to determine the chemical forms of iron present in leachates, extracts, and leachates to which iron salts were added. It was found that the major part of the iron in a maple leachate was not retained by either the cation or the anion exchange resin used, and that the behaviour of the iron retained by these resins suggested that it was held by adsorption or precipitation rather than by ion-exchange. When ferrous or ferric sulphate was added to a maple leachate it was found that most of the iron so added was retained by the resins. Precipitation and adsorption

appeared to play major roles in this retention. Iron extracted from calcareous till by maple leachate was not retained by the resins, but that similarly extracted from C-horizon sand was retained almost wholly. Conclusions respecting the chemical forms of iron present could not be drawn from these experiments.

Electrodialysis indicated that most of the iron (about 65 per cent) in a maple extract from C-horizon sand was cationic. However, only a minor part (less than 10 per cent) of the iron present in a maple leachate reacted with 2,2'-dipyridyl. Further, both ferrous and ferric ions added to maple leachate as their sulphates were incompletely recoverable (23 to 49 per cent) by reaction with this reagent after one-half hour of contact. It was concluded that maple leachate is capable of converting ionic iron to stable complexes or compounds.

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Note added in press:

Since this paper was submitted for publication it has been learned that the 2,2'-dipyridyl reaction for the estimation of ferrous iron (hydroxylamine not added) is unreliable in presence of the organic matter of leaf extracts. The ferrous iron content of such solutions is over-estimated. A brief communication respecting observations in this connection is in preparation for publication.

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